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Densities, viscosities, refractive indices, and electrical conductivities of aqueous alkali salts of α-alanine

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ABSTRACT

In this work, physicochemical properties such as density, viscosity, refractive index, and electrical conductivity of aqueous alkali (potassium or sodium) salts of the amino acid α-alanine (ALA), were measured at temperatures from (303.15 to 343.15) K and concentrations ranging from (0.5 to 3.5) M. Density and viscosity measurements were performed using the vibrating tube and the falling ball techniques, respectively. The refractive index at the sodium D line was measured in an automatic refractometer, while the electrical conductivity was measured using a commercial conductivity meter. An empirical equation was applied to correlate the density, refractive index, and electrical conductivity of the amino acid salt solutions with temperature and amino acid salt concentration, which gave average absolute deviation values of 0.03%, 0.01%, and 0.6%, respectively. The variation of the viscosity as a function of temperature and amino acid salt concentration was accurately represented by a modified Vogel–Tamman–Fulcher equation at an average absolute deviation of 0.5%.

1. Introduction

Aqueous amino acid salt solutions have emerged in recent years as attractive environment-friendly, energy-efficient alternatives to conventional aqueous alkanolamine absorbents for CO_2 capture [1–4]. Like alkanolamines, they contain amino groups, which allow them to have favorable binding capacity toward CO_2. They have been proposed to absorb CO_2 through the same mechanism as typical amines do. Primary and secondary amines (or amino acid salts) react with CO_2 forming stable carbamates while the reaction of a tertiary amine with CO_2 leads to bicarbonate formation [5]. But unlike alkanolamines, amino acid salts are stable in the presence of oxygen, which makes them resistant to oxidative degradation. Also, the ionic nature of an amino acid salt solution, which is formed from the neutralization of an amino acid with an alkaline hydroxide, makes it practically non-volatile [6]. Furthermore, CO_2 absorption in such solvent could lead to the formation of solid precipitates, which could cause the driving force to remain constant over a certain range of solution loadings. The loaded solvent containing the precipitates may be regenerated by increasing the temperature to drive off the CO_2 and re-dissolve the precipitated amino acid [7,8]. Although this phenomenon may pose a disadvantage in the operation of absorption columns, it could lead to higher total solvent loading, lower energy consumption during regeneration, and reduced contactor size [1,9]. An additional advantage of aqueous amino acid salt solutions is their high surface tension, which make them suitable for application in membrane contactors [9,10].

Aqueous amino acid salts solutions (containing Na or K ions) were found to have comparable or even higher absorption capacity and better chemical reactivity with CO_2 than aqueous alkanolamine solvents [2,11–14]. Among those that are under extensive investigation is the salt of α-alanine (ALA), a sterically hindered amino acid. Song *et al.* [13] recently examined the CO_2 absorption characteristics of some common amino acid salts and found that the potassium salt of ALA, along with serine and α-aminobutyric acid, showed relatively fast initial CO_2 absorption and desorption rates, resulting in high net cyclic capacity. Such results have been attributed to the smaller distances between amino and carboxyl groups and the presence of a bulky substituent in the amino acids. Also, compared to its counterpart, potassium β-alanine, potassium ALA has been shown to have a much higher net cyclic capacity for CO_2. The authors reported that the addition of small amounts of piperazine (PZ) to aqueous ALA enhanced the initial absorption rate, and the net cyclic capacity of the activated solvent was higher than that of aqueous MEA by at least 25%. In another study, Lim *et al.* [12] showed that the CO_2 loading capacity of aqueous

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potassium ALA solution (2.5 M) was higher than that of aqueous MEA and aqueous diethanolamine (DEA) with the same concentrations. They also showed that the enthalpy of absorption (at $T = 298$ K) of aqueous potassium ALA was lower than that of MEA. Hence, it has been proposed as a potential energy-efficient replacement to existing amine absorbents.

Physicochemical properties are necessary in the design of gas–liquid contactors and the evaluation of suitable absorbents for CO_2 capture. For aqueous ALA salt solutions, such properties have not yet been reported in the literature. Thus, in the present work, we presented new experimental data on density, ρ, viscosity, η, electrical conductivity, κ, and refractive index, n_D, of aqueous alkali (potassium or sodium) ALA salt solutions. Measurements were made for amino acid salt concentrations from (0.5 to 3.0) M and temperatures from (303.15 to 343.15) K. Another aim of this work was to represent the experimental values as a function of temperature and concentration using suitable correlations, which can be useful in calculations for the design of processes utilizing the studied solvents.

2. Experimental

2.1. Materials and amino acid salt preparation

The amino acid α-alanine (ALA, CAS No. 302–72-7, mass fraction purity > 0.99) was purchased from Alfa Aesar. The alkali hydroxides KOH (mass fraction purity > 0.85) and NaOH (mass fraction purity 0.9999) were supplied by Sigma Aldrich. All chemicals, which are described in Table 1, were used as received. The exact purities of KOH and NaOH were determined by titration with standard HCl (1.0 M, Scharlau). Titration was performed using a Metrohm 888 Titrando potentiometric titrator, which measured pH to an accuracy of ±0.003. The instrument was calibrated (using standard buffer solutions) before use.

The aqueous amino acid salt solutions were prepared by adding an equimolar amount of KOH or NaOH to the amino acid in a volumetric flask with water. High-purity deionized distilled water, which was processed in an in-house water purification module (Barnstead Thermolyne, model Easy Pure 1052) was used in all the experiments. The exact concentrations of the solutions were determined by potentiometric titration with standard HCl solution (1.0 M). The uncertainty of the measured molar concentrations is estimated to be ±0.5%.

2.2. Density measurement

Density measurements were performed using an Anton Paar SVM 3000 vibrating tube density meter. It had an integrated thermostat with cascaded Peltier elements and Pt thermometer and a low-thermal mass measuring cell (a U-shaped borosilicate glass tube), which enabled rapid changes and exact adjustments to the measuring temperature. The temperature was controlled to ±0.005 K of the set value, and the accuracy of the measured value was ±0.02 K. The densimeter was calibrated using dry air and distilled deionized water as standard fluids. The calibration was validated by measuring the ρ of a certified calibration standard (APS3, Paragon Scientific, Ltd.) at the measuring range considered in this work. The results, which are given in table 2, suggest that the measured densities agree well with the standard reference values [15] (AAD = 0.01%). For each sample, each measurement was repeated three to five times. The overall uncertainty of the density measurement are estimated to be $\pm 8 \cdot 10^{-4}\ \mathrm{g \cdot cm^{-3}}$.

2.3. Viscosity measurement

Viscosity measurements were done using an Anton Paar AMVn automated falling ball microviscometer, which we had describe in detail in our earlier work [16]. The viscometer had a built-in Pt-100 temperature sensor for temperature control and measurement (uncertainty of ±0.05 K). It allowed measurements for a wide range of viscosities (0.3 to 2500) mPa · s using different measuring systems. In the present work, measurements were performed using a capillary with diameter $d = 1.6$ mm, which was calibrated at various angles using distilled deionized water before use. The calibration was validated by measuring the viscosity of the standard fluid APS3, which we have chosen due to its similar viscosity range as the amino acid salts systems studied in the same temperature range. The results of the validation are given in table 2 where it can be observed that the average deviation between the measured and the reference data is reasonably low (AAD = 0.5%). Taking such results into account, the uncertainty of the measured viscosity was estimated to be ±1.0%. All measurements were done in three to five replicate runs.

2.4. Refractive index measurement

Refractive index measurements were done in an Anton Paar Abbemat WR automatic refractometer. The instrument was equipped with a built-in temperature control and measuring system, which consisted of an internal solid state Peltier thermostat fitted with two internal Pt100 platinum resistance temperature sensors. The uncertainty of the temperature measurement was ±0.03 K. Measurements and calibration were performed as described in our earlier work [17]. The estimated overall uncertainty of the refractive index measurement was $\pm 5 \cdot 10^{-5}$. All measurements were performed in three replicates.

2.5. Electrical conductivity measurement

The electrical conductivity of each sample was measured using a Suntex SC-170 conductivity meter operating with an AC current of 60 Hz frequency. The temperature of the system was controlled using a water bath and measurement was done using a CROPICO 3002 digital thermometer with an uncertainty of ±0.01 K. The conductivity meter was calibrated using standard KCl solution obtained from Merck. The details of the calibration procedure have been described in our previous work [18].

For each measurement, 3 mL of sample was used whose temperature was controlled by immersing the sample tube in a water bath. After every measurement, the conductivity cell was washed with deionized water and ethanol to remove any adhering sample, and was dried before using it in the next measurement. All

TABLE 1
Description of chemicals used in this work.

Chemical name	Source	Mass fraction purity	Molar mass	Purification method
DL-alanine (CAS No. 302-72-7)	Alfa Aesar	>0.98	89.09	None
KOH	Merck	>0.85	56.11	None
NaOH	Alfa Aesar	>0.9999	40.00	None
HCl (1.0 M)	Scharlau	Standard solution		